

# PATENT SPECIFICATION

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## (54) METHOD OF WASHING GLASSWARE AND CLEANING SOLUTION AND ADDITIVE COMPOSITION USEFUL THEREIN

(71) We, BASF WYANDOTTE CORPORATION, a corporation organized under the laws of the State of Michigan, United States of America, of 1609 Biddle Avenue, Wyandotte, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention broadly relates to the washing of glassware in aqueous strongly alkaline solutions. In one of its more specific variants, the invention is concerned with a method of washing soiled hot end coated glassware in an inhibited aqueous caustic soda cleaning solution whereby the resulting cleaned glassware may be recycled. The invention further relates to a novel aqueous caustic alkali cleaning solution and an additive composition which is especially useful in preparing and maintaining the same.

A variety of foods and beverages such as milk, soft drinks and beer are packaged in returnable glass bottles which are refilled and recycled a number of times during their normal life. When returnable bottles are emptied by the consumer and returned to the bottler for refilling they must be washed thoroughly to remove all soil or other residues and thereby render the bottles physically clean. It is also necessary to sterilize the bottles and remove all microbial contamination. The most suitable washing solutions in use at the present time are highly alkaline aqueous solutions of alkali metal hydroxide. Sodium hydroxide is usually lower in cost and is preferred. Other ingredients which may be present include alkali metal carbonates, orthophosphates, pyrophosphates, polyphosphates, silicates, and borates, and various surface active agents.

The surface of glassware which is washed repeatedly in the above described solutions is subject to alkali attack. This is especially pronounced in instances where returnable bottles are washed in a mechanical soaker-washer machine and contacted therein with a heated washing solution over a number of cycles. As a result, the defaced glass surfaces take on a scratched, etched or worn appearance which is often initiated by mechanical abrasion and then accentuated by alkali attack. The term "scuffing" is commonly used to describe the pitting, knicking, scratching, wear and general defacement of the surfaces of glassware containers through the combined forces of mechanical abrasion, chemical corrosion and weathering.

Glass derives its strength from an unblemished surface and any flaws therein decrease the strength to only a fraction of the original value. Scuffing reduces the strength of glass bottles and renders them more liable to breakage during handling and in the case of carbonated beverages, explosion following filling and crowning. As a result, a number of efforts have been made heretofore to reduce scuffing to a minimum.

One of the most successful methods of reducing scuffing is by hot end coating the glassware with a substantially colorless and transparent thin protective coating including at least one organic coating material which is applied to the glass surface while hot. In accordance with one variant of the hot end coating method, the surface of the glassware is spray d with a dilute solution or aqueous emulsion of the organic coating material such as polyethylene and/or an alkali metal salt of a

2 fatty acid at an elevated temperature which is below the annealing temperature to  
thereby deposit a tightly adherent abrasion resistant organic film. In accordance  
with one preferred variant, the glass surface is provided with a thin transparent,  
substantially colorless dual protective coating which has outstanding abrasion  
5 resistant properties. The coating immediately adjacent the glass surface is a layer  
of a metal oxide and the second layer is an organic coating material which is  
applied thereover and bonded thereto. In one of the most preferred variants, a first  
layer of tin, zirconium or titanium oxide is pyrolyzed onto the hot glass surface,  
10 and a dilute aqueous emulsion of polyethylene or a mixture of polyethylene and an  
alkali metal salt of a fatty acid is applied over the first layer and bonded thereto  
while the glass surface is still hot. 10

Hot end coated glassware is much stronger and abrasion resistant initially  
than uncoated glassware. However, hot end coated glassware does have one  
severe deficiency in that when it is cleaned repeatedly in conventional soaker-  
15 washers using highly alkaline cleaning solutions, there is a very objectionable  
discoloration and a marked loss of lubricity. Apparently at least the outer organic  
protective coating layer is altered and/or either partially or completely removed by  
the repeated washings and the washing solution is then free to attack the inner  
metal oxide layer when present. The discoloration is unsightly and not acceptable  
20 to the bottling industry from the esthetic standpoint. The loss of lubricity renders  
the glass surface subject to scuffing as was true of the uncoated glass surfaces of  
the prior art. A suitable method of effectively overcoming the foregoing deficiency  
of hot end coated glassware was not available prior to the present invention in  
spite of the great need therefore. 20

25 According to the present invention there is provided a liquid additive  
composition for an aqueous caustic alkali cleaning solution comprising a  
homogeneous aqueous solution containing dissolved therein, on a weight basis,  
from 2.5% to 35% of caustic alkali, from 0.5% to 7% of at least one water-soluble  
zinc-containing compound, calculated as zinc oxide, from 0.2% to 2.7% of at least  
30 one synthetic organic phosphate ester anionic surfactant having hydrotrophic  
properties, from 0.06% to 0.8% of at least one synthetic alkoxyated nonionic  
surfactant, and from 1% to 14% of at least one hard water conditioning  
sequesterant. 25

35 The invention also provides an aqueous caustic alkali cleaning solution  
containing an amount of additive composition according to the invention to  
provide the zinc-containing compound in a concentration of from 0.01 to 0.3% by  
weight, calculated as zinc oxide. 35

40 The invention further provides a method of washing hot end coated glassware  
having a substantially colorless and transparent thin protective coating thereon  
including at least one organic coating material applied to the glassware while hot  
comprising washing the said hot end coated glassware in an aqueous caustic  
cleaning solution according to the invention. 40

45 The method of the invention preserves the desirable protective properties and  
appearance of the coating. As a result, the unsightly discoloration and loss of  
lubricity characteristic of repeated washings of hot end coated glassware is  
strongly alkaline aqueous solutions is prevented. The coating remains colorless  
and transparent without a serious loss of lubricity, and the glassware retains its  
initial high strength and pleasing appearance. The soluble zinc-bearing substance  
50 dissolved in the cleaning solution inhibits the deleterious effects of the washing  
solution on the outer organic coating, and ultimately upon the inner metal oxide  
coating when present. 50

All references made hereinafter to quantities or percentages of the  
ingredients used in preparing the additive composition or the washing solution are  
by weight unless otherwise indicated.

55 The washing solution generally contains from 0.3% to 6% of caustic alkali, and  
preferably 2% to 4%. The best results are usually achieved when caustic soda is  
present in a concentration of approximately 3%. Caustic soda, i.e. sodium  
hydroxide, is available commercially in large quantities and is usually the preferred  
caustic alkali due to its lower cost. It is to be understood that other alkali metal  
60 hydroxides such as potassium hydroxide may be present when desired instead of or  
in addition to caustic soda. 60

65 The washing solution contains an inhibitor which markedly reduces the rate at  
which the caustic alkali attacks the protective coating on the glassware. The  
inhibitor is a water-soluble zinc-containing compound which is dissolved in the  
washing solution in an amount to provide from 0.01% to 0.3%, calculated as zinc 65

oxide, and preferably 0.03% to 0.1%. The best results are often achieved when the washing solution contains the zinc compound in an amount of approximately 0.06%, calculated as zinc oxide.

5 The specific zinc-bearing substance to be added to the washing solution and/or dissolved in a strongly alkaline aqueous medium and then added thereto, is not of importance provided the substance is capable of being solubilized as a zincate. The zinc-bearing substance may be metallic zinc or a suitable zinc-containing compound, for example zinc chloride, zinc sulfate, zinc nitrate, zinc phosphate, 10 zinc oxide, sodium zincate or potassium zincate. Mixtures of two or more of the zinc-bearing substances may be used. Zinc oxide is usually preferred, especially in the form of a finely divided powder which dissolves rapidly. The zinc-bearing substance may be added to the washing solution or other strongly alkaline aqueous medium and dissolved therein. Room temperature is often satisfactory in the presence or absence of agitation but the dissolution proceeds at a faster rate with 15 agitation and when using an elevated temperature such as 50—100°C. The dissolution step is continued until the zinc-bearing substance is in solution.

Regardless of the initial source, the zinc is present as the alkali metal zincate, e.g., sodium zincate, upon dissolution and admixing in the strongly alkaline washing solution.

20 The amount of zinc source to be added and the amount of the zinc compound in the washing solution are calculated on a weight basis as zinc oxide, as distinguished from the initial metallic zinc or zinc compound or the solubilized alkali metal zincate.

25 The source of the water that is used in preparing the washing solution is not of importance provided deleterious impurities are not present. For example, the water may be tap water from a municipal water supply, distilled water, deionized water, and the like. The water is present in the quantity necessary to provide the aforementioned concentrations of ingredients in the washing solution.

30 In addition to the above mentioned ingredients, the washing solution also contains certain types of anionic surfactant, nonionic surfactant and sequestering agent. The anionic surfactant is dissolved therein in an amount generally from 0.002% to 0.05% and preferably from 0.01% to 0.03%. The nonionic surfactant is present in an amount generally from 0.001% to 0.03%, and preferably from 0.005% to 0.01%. The sequestering agent is present in an amount generally from 0.008% to 0.2%, and preferably from 0.03% to 0.1%. The best results are usually obtained 35 when the washing solution contains approximately 0.013% of the anionic surfactant, 0.007% of the nonionic surfactant, and 0.06% of the sequestering agent.

The anionic surfactant comprises at least one synthetic organic phosphate ester having hydrotrophic properties. A large number of such synthetic organic phosphate ester anionic surfactants are known and may be selected by one skilled in this art for use in the present invention. The phosphate esters of various hydroxylic organic compounds may be used. The alkylphenol polyglycol ether phosphates are very satisfactory and may be used advantageously. The presently preferred synthetic organic phosphate ester anionic surfactant is more particularly 45 described in United States Patent No. 3,235,627. A product marketed commercially by Rohm and Haas under the trade-mark "Triton H-66" gives exceptionally good results. In its commercial form, Triton H-66 is the potassium salt of an alkylphenol polyglycol ether phosphate which is sold as a 50% solids aqueous solution, and which is further characterized by a viscosity of 120 centipoises at 25°C, a specific gravity of 1.26, a pH of 8—10 in 5% aqueous solution, and a freezing point of -20°C. Other metal salts and ammonium salts of the foregoing class of anionic surfactants may be used and especially the sodium potassium and ammonium salts.

50 Another phosphate ester anionic surfactant which may be employed is the phosphate ester of the nonionic surfactant represented by the formula:

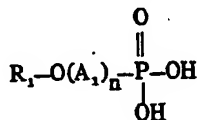


60 where R is an alcoholic residue or alkyl group having from 10 to 18 carbon atoms or mixtures thereof, A is either oxyethylene groups or a mixture of oxyethylene and oxypropylene groups in an ethylene oxide to propylene oxide weight ratio of from 0.5:1 to 6:1, and n is an integer sufficiently large to ensure that A constitutes from 40 to 85% of the total weight of the surfactant.

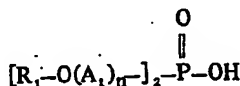
As is known in the art, when a mixture of compounds of the type used herein is employed there is generated a series of closely related homologs having varying

oxyalkylene chain lengths. Thus, the values indicated above are average values. Typical of these nonionic surfactants are those disclosed and claimed in U.S. Pats. Nos. 3,340,309; 3,504,041; and Canadian Pat. No. 770,644.

The phosphate ester anionic surfactant may be prepared by reacting a nonionic surfactant with polyphosphoric acid. Generally, the polyphosphoric acid is used in excess over stoichiometric requirements. The phosphate ester obtained by this reaction is, rather, a mixture of mono- and diesters corresponding to the formulae:



and



where  $R_1$ ,  $A_1$  and  $n$  have the meanings ascribed to  $R$ ,  $A$  and  $n$ , above, and wherein the mixture comprises from 60 to 100% by weight of monoester and from 40 to 0% by weight of diester and  $A_1$  constitutes from about 30 to 80% of the total weight of the ester.

The nonionic surfactants to be used are low foaming synthetic alkoxyated nonionic surfactants. Examples of alkoxyated nonionic synthetic detergents which may advantageously be employed include polyoxyalkylene adducts of hydrophobic bases. Ethylene oxide, for example, is condensed with the hydrophobic base in an amount sufficient to impart water solubility and surface active properties to the molecule being prepared whilst still rendering the product low foaming. The exact amount of ethylene oxide condensed with the hydrophobic base will depend upon the chemical characteristics of the base employed and is readily apparent to those of ordinary skill in the art relating to the synthesis of oxyalkylene surfactant condensates. In general, the amount of ethylene oxide is less than 20% of the weight of the hydrophobic base for low foaming products.

Typical hydrophobic bases which can be condensed with ethylene oxide in order to prepare nonionic surface active agents include mono- and polyalkyl phenols and the compounds prepared by condensing polyoxypropylene onto a base having from 1 to 6 carbon atoms and at least one reactive hydrogen atom. The hydrocarbon ethers such as the benzyl or lower alkyl ether of the polyoxyethylene surfactant condensates are also advantageously employed in the compositions of the invention.

Further suitable nonionic surface active agents are the polyoxyethylene esters of higher fatty acids having from 8 to 22 carbon atoms in the acyl group. Typical products are the polyoxyethylene adducts of tal oil, rosin acids, lauric, stearic and oleic acids and the like. Additional nonionic surface active agents are the polyoxyethylene condensates or higher fatty acid amines and amides having from 8 to 22 carbon atoms in the fatty alkyl or acyl group. Illustrative products are coconut oil, fatty acid amines and amides condensed with ethylene oxide.

Other suitable polyoxyethylene nonionic surface active agents are the ethylene oxide adducts of higher aliphatic alcohols and thioalcohols having from 8 to 22 carbon atoms in the aliphatic portion. A typical product is tridecyl alcohol condensed with ethylene oxide.

Other suitable nonionic surface active agents are cogeneric mixtures of conjugated polyoxyalkylene compounds containing in their structure at least one hydrophobic oxyalkylene chain in which the oxygen/carbon atom ratio does not exceed 0.40 and at least one hydrophilic oxyalkylene chain in which the oxygen/carbon atom ratio is greater than 0.40. In accordance with the preferred practice of this invention, the hydrophilic oxyalkylene chain is less than 20% of the total weight of the oxyalkylene chains.

Polymers of oxyalkylene groups obtained from propylene oxide, butylene oxide, amylene oxide, styrene oxide, mixtures of such oxyalkylene groups with each other and with minor amounts of polyoxyalkylene groups obtained from ethyl n oxide, butadiene dioxide, and glycidol are illustrative of hydrophobic

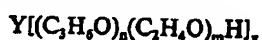
oxyalkylene chains having an oxygen/carbon atom ratio not exceeding 0.40. Polymers of oxyalkylene groups obtained from ethylene oxide, butadiene dioxide, glycidol, mixtures of such oxyalkylene groups with each other and with minor amounts of oxyalkylene groups obtained from propylene oxide, butylene oxide, amylene oxide and styrene oxide are illustrative of hydrophilic oxyalkylene chains having an oxygen/carbon atom ratio greater than 0.40.

Among the conjugated polyoxyalkylene compounds which may be used are those which correspond to the formula



wherein Y is the residue of an organic compound having from 1 to 6 carbon atoms and one reactive hydrogen atom, n has an average value of at least 6.4 as determined by hydroxyl number and m has a value such that the oxyethylene portion constitutes up to 20 weight percent of the molecule. These surface active agents are more particularly described in U.S. Pat. No. 2,677,700.

Other conjugated polyoxyalkylene surface active agents which are most advantageously used correspond to the formula:



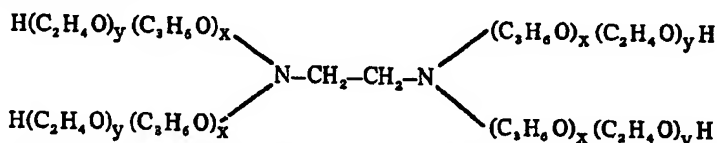
wherein Y is the residue of an organic compound having from 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least 900 and m has a value such that the oxyethylene content of the molecule is up to 20 weight percent. Compounds falling within the scope of the definition for Y include, for example, propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylene diamine, and the like. As already noted, the oxypropylene chains optionally, but advantageously, contain small amounts of ethylene oxide and the oxyethylene chains also optionally, but advantageously, contain small amounts of other alkylene oxides such as propylene oxide and butylene oxide.

The polyoxypropylene-polyoxyethylene block copolymers useful as low foaming nonionic surfactants include compounds corresponding to the structural formula:



having a molecular weight of from 900 to 4500 and wherein a and c have values such that the ethylene oxide residues comprise from zero to 20% by weight of the total molecular weight of the copolymer. Copolymers of this type are usually prepared by condensing ethylene oxide with polypropylene glycol, polypropylene glycol in turn being the condensation reaction product of propylene oxide and propylene glycol. These compositions are more particularly described in U.S. Patent No. 2,674,619.

Other suitable nonionic surface active agents include ethoxylated and propoxylated adducts of ethylenediamine of a type generally described in U.S. Patent No. 2,979,528 but restricted to compounds exhibiting low foaming characteristics such as nonionic surfactants corresponding to the following structural formula:



where x and y are integers having values which ensure that the ethylene oxide residues constitute a maximum of 20% by weight of the total molecular weight of the surfactant and that the molecular weight of the adduct is from 900 to 1800. Compounds of this type may be prepared by the sequential addition of propylene oxide and ethylene oxide to ethylene diamine under oxyalkylation conditions.

Especially suitable alkoxylated linear aliphatic alcohols may contain 8-20 carbon atoms and preferably 12-18 carbon atoms, and the alkylene oxide residues may comprise 5-40% by weight and preferably about 10-20% by weight of the molecule. The linear aliphatic alcohols are preferably ethoxylated and/or propoxylated under prior art alkoxylation conditions.

Additional low foaming nonionic surface active agents are disclosed in United States Patents Nos. 3,425,755, 3,340,309, 3,504,041 and 3,770,701.

The various types of nonionic surfactants disclosed herein may be used individually or admixtures thereof may be employed. Exemplary admixtures comprise a weight ratio of the above described ethoxylated and propoxylated adduct of ethylenediamine to one or more of the remaining nonionic surfactants ranging from about 2:1 to 1:2, and preferably about 1:1 may be employed.

The sequesterant is of the type used in conditioning hard water. A wide variety of hard water conditioning sequesterants are known and may be selected by one skilled in this art for use in practicing the present invention, for example ethylenediamine tetraacetic acid, nitrilotriacetic acid, the sugar acids, and the ammonium salts and metal salts thereof. Usually the sodium, potassium and ammonium salts are preferred. Other substances which may be used include the phosphates, pyrophosphates, polyphosphates, etc. The presently preferred sequestering agents are  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , -amino tris(methyl phosphonic acid), the sugar acids and/or the ammonium and metal salts thereof, of which the sodium, potassium and ammonium salts are preferred. The term "sugar acid" as used herein refers to the fermentation acids as well as the aldonic and dibasic acids produced from sugars by chemical oxidation. Examples of this class of acids include lactic acid, citric acid, gluconic acid, 2-ketogluconic acid, glucoheptonic acid, tartaric acid, arabinic acid, galactonic acid, saccharic acid, mucic acid, and the like. Typical alkali metal salts of the sugar acids include sodium lactate, sodium citrate, potassium sodium tartrate, sodium arabinonate, sodium gluconate, sodium galactonate, sodium 2-ketogluconate, potassium sodium saccharate, sodium mucate and sodium glucoheptonate. The above compounds and their use as sequestering agents is more particularly described by Mehlretter, et al, Industrial and Engineering Chemistry, Vol. 95, No. 12, December, 1953, pages 2782, et. seq. Sodium gluconate and/or sodium glucoheptonate are the presently preferred salts of the sugar acids.

A mixture of two or more of the above classes of sequestering agents often gives better results. The presently preferred mixture of sequestering agents has a weight ratio of (1) at least one sugar acid and/or an alkali metal or ammonium salt thereof to (2)  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , -amino tris(methyl phosphonic acid) and/or a sodium, potassium or ammonium salt thereof of from 15:1 to 25:1, and for best results 18:1 to 22:1.

The novel washing solution and additive composition for use in preparing and maintaining the same have a synergistic combination of ingredients which contribute both to the low foaming characteristics and enhanced inhibition. Thus, much better results are achieved by washing the glassware in a washing solution having the composition (excluding water) set out below than in a solution containing only caustic soda, the zinc-containing compound and water:

Weight %

Ingredient	Broad Range	Preferred Range	Optimum Amount
Caustic Soda	0.3-6	2-4	3
Zinc Compound (Zinc Oxide)	0.01-0.3	0.03-0.1	0.06
Anionic Surfactant	0.002-0.05	0.01-0.03	0.013
Nonionic Surfactant	0.001-0.03	0.005-0.01	0.007
Sequesterant	0.008-0.2	0.03-0.1	0.06
Water preferably constitutes the entire remainder.			

The novel additive of the invention has the following composition, excluding water, which preferably constitutes the entire remainder:

## Weight %

Ingredient	Broad Range	Preferred Range	Optimum Amount
Caustic alkali, preferably caustic soda	2.5-35	15-20	18
Zinc Compound (as Zinc Oxide)	0.5-7	2-5	3.5
Anionic Surfactant	0.2-2.7	0.5-1	0.8
Nonionic Surfactant	0.06-0.8	0.2-0.6	0.4
Sequesterant	1-14	2-5	3.6

It is to be understood that the zinc-containing compound in the above washing solution and additive composition is calculated as zinc oxide as previously mentioned. Also, the various ingredients are as previously mentioned in discussing the method of the invention.

The washing solution and additive composition may be prepared by merely admixing the ingredients together in the prescribed amounts. The zinc-bearing substance may be dissolved as discussed hereinbefore and then admixed with the remaining ingredients. Ambient temperature conditions are usually satisfactory, but elevated temperature may be used such as 50-100°C. In general, no special handling procedures are necessary.

The additive composition may be used when preparing the washing solution initially and/or it may be used for making additions to maintain the concentrations of ingredients at the desired levels. When preparing the washing solution initially, the additive composition is admixed with water in an amount to provide the desired amount of the zinc-containing compound in the final solution and the caustic soda level is adjusted as necessary by adding concentrated aqueous caustic alkali or caustic alkali in flake form. The additive composition is formulated to provide the proper ratio of all ingredients in the washing solution with the possible exception of the caustic alkali (caustic soda). Thus increments of the additive composition and additional caustic alkali may be added to an existing washing solution in the quantities necessary to maintain the desired concentrations of ingredients.

The washing solution may be used for washing soiled hot end coated glassware in accordance with prior art techniques. As a general rule, it is only necessary to substitute the washing solution of the present invention for a prior art caustic alkali washing solution. In instances where the hot end coated glassware is in the form of returnable beverage bottles, then a mechanical washing machine of the soaker-washer type or the hydraulic type may be used. A soaker-washer machine known in the art as Meyer Dumore Model No. 524PT is very satisfactory and a typical prior art operating cycle therefor may be used. The operating cycle usually includes passing the bottles successively through a series of five tanks which are filled with cleaning or rinsing solutions. The returned soiled bottles usually are washed with warm water followed by soaking at approximately 130-140°F in a washing solution containing 3-3.5% of caustic soda, followed by soaking at approximately 160-175°F in a washing solution containing about 2.5-3% of caustic soda, followed by a further soaking cycle at about 145-155°F in a solution containing 1-2% of caustic soda. The soaking cycles are usually followed by aqueous rinsing cycles at lower temperatures, such as a temperature of 80-100°F in a first rinse tank, followed by a temperature of 60-70°F in a second rinse tank. Thereafter the bottles may be brushed internally and externally to remove any adherent deposits followed by one or more internal and external fresh water rinses. The cleaned and rinsed bottles may be given internal and external chlorination rinses for the purpose of killing any microbes which may be present.

It is understood that the number and sequence of the cleaning and rinsing steps is dependent to some extent upon the nature of the foreign substances on the soiled bottles and the extent of the soiled articles. A practical range of temperature



for the soaking step is about 120—180°F. and preferably about 160—170°F. Usually lower temperatures require longer soaking periods, whereas higher temperatures require shorter soaking periods. As a general rule, the period of exposure to the washing solution is about 2—10 minutes in each soaking step, and preferably about 4—5 minutes.

The hot end coated glassware to be washed in accordance with the method of the invention may be in the form of glasses, tumblers, bottles, cups, jars, plates, and the like. The method is especially effective in instances where the glassware is of the returnable type and therefore subjected to a plurality of washings in a highly alkaline caustic soda solution during its normal life span. Returnable bottles of the types employed in the milk, soft drink and brewing industries are the most important from the commercial standpoint, but the invention also has utility in other fields. In instances where the hot end coated glassware is washed a number of times in the caustic soda washing solutions of the prior art, then the outer protective organic coating is partially or completely removed and the caustic soda solution is free to attack the inner metal oxide coating when present.

An unsightly discoloration develops which renders the glassware unacceptable from the esthetic standpoint and especially when used as a container for food and beverages. Additionally, once the protective coating is removed the abrasion resistance drops markedly and the glassware is subject to scuffing and loss of strength as was characteristic of the prior art uncoated glassware. The method of the present invention increases the effective life of the protective coating by at least five fold and often even longer, and thus the useful life of the glassware is increased by an equal amount.

The preparation of hot end coated glassware is described in a number of United States Patents, including the following:

2,995,533	3,352,708	3,407,085
3,352,707	3,368,915	3,441,399
		3,743,491

In general, the above patents disclose methods of providing glassware with a protective coating shortly after the molten glass has been solidified into the shape of the article being manufactured. The surface of the glass is still hot, and the heat content thereof is utilized in the protective coating step to deposit the protective film and cause the same to adhere tightly to the glass surface. In one variant, only an organic protective coating is applied to the glass surface. In a further variant, a dual protective coating is applied which comprises an inner metal oxide layer and an outer organic layer.

The single protective coating variant is illustrated in United States Patent No. 2,995,533. In accordance with the method of this patent, the abrasion resistance and strength of the glassware is increased by spraying an aqueous emulsion containing polyethylene and an alkali metal fatty acid salt on the hot glass surface. At the time of applying the aqueous emulsion, the glassware surface is at a sufficiently elevated temperature to result in the immediate evaporation of the water component of the emulsion and to obtain a tight adherence of the polyethylene particles to the glass surface. A temperature of approximately 400°F. is satisfactory. It is preferred that the aqueous emulsion be sprayed onto the surface of the glassware in controlled quantities to allow rapid evaporation of the water content and cause an extremely tight adherence of the polyethylene particles to the glass surface in the form of a thin invisible protective organic film.

In the presently preferred commercial practice, the glassware surface is provided with a thin transparent, substantially colorless dual protective coating. The inner protective coating layer is a metal oxide layer which is formed by pyrolyzing a heat decomposable organic compound of the desired metal on the hot glass surface. A wide variety of metal oxides may be applied, such as tin, zirconium, titanium, aluminum, vanadium, germanium, iron, cobalt, nickel, zinc, lead, and the like. Usually an oxide of tin, zirconium or titanium is preferred. The glass surface is sufficiently hot at the time of applying the metal bearing compound to cause the immediate decomposition thereof and the deposition of an oxide of the metal which adheres tightly to the glass surface. Thereafter, a solution or aqueous emulsion of an organic coating material is applied while the glass surface is still hot following the general technique previously described for the single protective coating variant. Examples of organic coating materials which may be applied include olefin polymers such as polyethylene and polypropylene, poly-



amides, poly esters, polyvinyl alcohol, copolymers of ethylene and ethylenically unsaturated carboxylic acids, polybutadiene, copolymers of vinylchloride and vinyl acetate, polyurethanes, organopolysiloxanes and carnauba wax. The resulting outer layer of an organic protective coating is applied over the metal oxide layer, and it adheres tightly and is bonded thereto. The dual protective coating imparts excellent abrasion resistance and is much more durable and lasting, and especially when the metal oxide is tin oxide and the organic coating comprises polyethylene. Examples of the dual coating variant are disclosed in U.S. Patents No. 3,368,915, 3,407,085, and 3,743,491.

Protective coatings on glassware of the types disclosed in the aforementioned patents are generally known and referred to in this art as "hot end coatings", and the glassware produced by such coating processes is commonly referred to as "hot end coated glassware". These art accepted terms are therefore adopted and used herein in the specification and claims.

The following specific examples further illustrate the invention. All references to quantities or percentages are by weight unless otherwise indicated.

#### EXAMPLE I.

This example illustrates the washing of hot end coated glassware in accordance with the method of the invention.

Hot end coated returnable soft drink bottles were washed in this example. The bottles were coated with a dual protective coating including a tin oxide undercoating and a polyethylene organic coating applied thereover and bonded thereto.

The bottles were washed in a Meyer Dumore Model No. 524 PT Soaker-Washer which had five tanks arranged in series. The first three of the five tanks were filled with washing solutions having varying concentrations of ingredients and the last two tanks were aqueous rinsing tanks. The general washing technique that was employed was in accordance with prior art practice for a soaker-washer of this type with the exception of using the washing solution of the present invention.

The concentrations of ingredients in the five soaker-washer tanks and the operating temperature are given below:

Ingredients (Wt %) Operating Temperatures (°F)	Soaker-Washer Tank No.				
	1	2	3	4	5
Caustic Soda	3.3	2.8	1.5	0.3	trace
Zinc Compound (Zinc Oxide)	0.06	0.06	0.05	0.04	0.01
Anionic Surfactant <sup>1</sup>	0.013	0.013	0.01	0.006	0.002
Nonionic Surfactant <sup>2</sup>	0.007	0.007	0.006	0.004	0.001
Sequestering Agent <sup>3</sup>	0.06	0.06	0.05	0.03	0.01
Water	remainder	remainder	remainder	remainder	remainder
Operating temperature	130-136	160-172	144-152	80-100	60-70

<sup>1</sup> The anionic surfactant was Triton H-66, which is an alkylphenol polyglycol ether phosphate in potassium salt form having a viscosity of 120 centipoises at 25°C., a specific gravity of 1.26, a pH of 8-10 in 5% aqueous solution and a freezing point of -20°C.

<sup>2</sup> The nonionic surfactant was an ethoxylated adduct of the condensation product of ethylene diamine and propylene oxide having an average molecular weight of from 2750 to 3350 and containing about 10% by weight of ethylene oxide residues.

<sup>3</sup> The sequestering agent was a mixture of (a) sodium glucoheptonate and (b)  $\alpha, \alpha', \alpha''$ -amino tris-(methyl phosphonic acid) in a weight ratio of (a) to (b) of 20:1.

The overall time required for the bottles to make one trip through the soaker-washer was 20—25 minutes. Thus, the bottle residence time in each of the five tanks was approximately 4—5 minutes.

The test bottles were recycled through the soaker-washer for a total of 25 trips. Representative samples of the test bottles were retained after each five trips through the washer up to and including the twenty-fifth trip, i.e., for the fifth, tenth, fifteenth, twentieth and twenty-fifth trips. After the twenty-fifth trip, a sample from each group of the representative samples of the bottles was placed in the first soaker-washer tank and allowed to remain therein for one half-hour with the machine stopped. This static soak was for the purpose of observing the effects of prolonged exposure to the highly alkaline caustic soda solution of Tank No. 1.

Upon testing and evaluating the various sample bottles prepared by the above procedure, the protective films thereon were found to be intact. The bottles still exhibited good lubricity characteristics and there was no indication of discoloration or loss of strength. Thus, the method of the invention is capable of prolonging the effective life of the protective coating over at least twenty-five recyclings.

#### EXAMPLE II.

This example illustrates the detrimental effects of washing hot end coated soft drink bottles in caustic soda solutions in accordance with prior art practice.

The general procedure of Example I was repeated in this example with the exception of omitting the zinc compound, the anionic surfactant, the nonionic surfactant and the sequestering agent from the washing solution. Thus, the washing solution contained only caustic soda and water in the concentrations noted therefor in Example I.

The bottles were discolored after completing five trips through the soaker-washer. Upon further examination and testing, it was found that the protective coating was altered and/or removed and was no longer capable of protecting the bottle surfaces. Scuffing and loss of strength resulted therefrom in addition to discoloration after the equivalent of only five recyclings. Inasmuch as the average life of returnable beverage bottles is approximately 15 recyclings, it is apparent that the useful life of the hot end coated bottles is shortened due to washing in the uninhibited caustic soda cleaning solutions of the prior art.

#### WHAT WE CLAIM IS:—

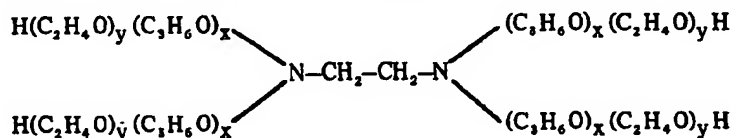
1. A liquid additive composition for an aqueous caustic alkali cleaning solution comprising a homogeneous aqueous solution containing dissolved therein, on a weight basis, from 2.5% to 35% of caustic alkali, from 0.5% to 7% of at least one water-soluble zinc-containing compound, calculated as zinc oxide, from 0.2% to 2.7% of at least one synthetic organic phosphate ester anionic surfactant having hydrotrophic properties, from 0.06% to 0.8% of at least one low foaming synthetic alkoxylated nonionic surfactant, and from 1% to 14% of at least one hard water conditioning sequesterant.

2. An additive composition as claimed in Claim 1 wherein the caustic alkali is caustic soda present in an amount from 15% to 20%, the zinc-containing compound is present in an amount from 2% to 5%, calculated as zinc oxide, the anionic surfactant is present in an amount from 0.5% to 1%, the nonionic surfactant is present in an amount from 0.2% to 0.6% and the sequesterant is present in an amount from 2% to 5%, all percentages being by weight of the aqueous solution.

3. An additive composition as claimed in Claim 1 or 2 wherein the anionic surfactant is an alkylphenol polyglycol ether phosphate or an alkali metal or ammonium salt thereof.

4. An additive composition as claimed in any of Claims 1 to 3 wherein the sequesterant is a mixture comprising (1) at least one sugar acid and/or an alkali metal or ammonium salt thereof, and (2)  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ -amino tris-(methyl phosphonic acid) and/or an alkali metal or ammonium salt thereof, at a weight ratio of (1) to (2) of from 15:1 to 25:1.

5. An additive composition as claimed in any of Claims 1 to 4 wherein the nonionic surfactant is a polyoxyethylene-polyoxypropylene adduct of ethylenediamine corresponding to the structural formula



where x and y are integers of numerical values to ensure that the ethylene oxide residues constitute a maximum of 20% by weight of the total weight of the molecule and that the molecular weight of the adduct is from 900 to 7800.

- 5      6. An additive composition as claimed in any of Claims 2 to 6 wherein the caustic soda is present in an amount of about 18%, the zinc-containing compound is present in an amount of about 3.5%, calculated as zinc oxide, the anionic surfactant is present in an amount of about 0.8%, the nonionic surfactant is present in an amount of about 0.4%, and the sequesterant is present in an amount of about 3.6%, all percentages being by weight of the aqueous solution.      5
- 10     7. An additive composition as claimed in any of Claims 1 to 6 in which the remainder apart from the specified ingredients is water.      10
- 15     8. An additive composition as claimed in Claim 1 and substantially as hereinbefore specifically described or exemplified.      15
- 20     9. An aqueous caustic alkali cleaning solution containing an additive composition as claimed in any of Claims 1 to 8 in an amount to provide the zinc-containing compound in a concentration of from 0.01 to 0.3% by weight, calculated as zinc oxide.      20
- 25     10. An aqueous caustic alkali cleaning solution as claimed in Claim 9 wherein the zinc-containing compound is present in an amount from 0.03% to 0.1% by weight.      25
- 30     11. An aqueous caustic alkali cleaning solution containing the additive composition claimed in claim 6 in an amount to provide the zinc-containing compound in a concentration of about 0.06% by weight, calculated as zinc oxide.      30
- 35     12. An aqueous caustic soda cleaning solution comprising, on a weight basis, from 0.3% to 6% of caustic soda, from 0.01% to 0.3% of at least one water-soluble zinc-containing compound, calculated as zinc oxide, from 0.002% to 0.05% of at least one synthetic organic phosphate ester anionic surfactant having hydrophobic properties, from 0.001% to 0.03% of at least one low foaming synthetic alkoxylated nonionic surfactant and from 0.008% to 0.2% of at least one hard water conditioning sequesterant.      35
- 40     13. An aqueous caustic soda cleaning solution as claimed in Claim 12 wherein the caustic soda is present in an amount from 2% to 4%, the zinc-containing compound is present in an amount from 0.03% to 0.1%, calculated as zinc oxide, the anionic surfactant is present in an amount from 0.01% to 0.03%, the nonionic surfactant is present in an amount from 0.005% to 0.01% and the sequesterant is present in an amount from 0.03% to 0.1%, all percentages being by weight of the cleaning solution.      40
- 45     14. An aqueous caustic soda cleaning solution as claimed in Claim 12 or 13 wherein the anionic surfactant is as specified in Claim 3, the sequesterant is as specified in Claim 4 and/or the nonionic surfactant is as specified in Claim 5.      45
- 50     15. An aqueous caustic soda cleaning solution as claimed in any of Claims 12 to 14 wherein the caustic soda is present in an amount of about 3%, the zinc-containing compound is present in an amount of about 0.06%, calculated as zinc oxide, the anionic surfactant is present in an amount of about 0.013%, the nonionic surfactant is present in an amount of about 0.007% and the sequesterant is present in an amount of about 0.06%, all percentages being by weight of the cleaning solution.      50
- 55     16. An aqueous caustic soda cleaning solution as claimed in any of Claims 12 to 15 wherein the remainder, apart from the specified ingredients, is water.      55
17. An aqueous caustic soda cleaning solution as claimed in Claim 9 or 12 and substantially as hereinbefore specifically described or exemplified.
18. A method of washing hot end coated glassware having a substantially colorless and transparent thin protective coating thereon including at least one organic coating material applied to the glassware while hot comprising washing the said hot end coated glassware in an aqueous caustic cleaning solution as claimed in any of claims 9 to 17.
19. A method as claimed in Claim 18 wherein the organic coating material applied to the glassware comprises polyethylene.

20. A method as claimed in Claim 18 or 19 wherein the protective coating on the glassware includes a metal oxide layer applied to the surface of the glassware while hot and a layer of the organic coating material applied over the metal oxide layer and bonded thereto.

5 21. A method as claimed in Claim 20 wherein the metal oxide comprises tin oxide and the organic coating material comprises polyethylene. 5

22. A method as claimed in Claim 18 carried out substantially as hereinbefore specifically described or exemplified.

J.Y. & G.W. JOHNSON,  
Furnival House,  
14—18 High Holborn,  
London WC1V 6DE.  
Chartered Patent Agents.  
Agents for the Applicants.

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